

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**



The
Patent
Office

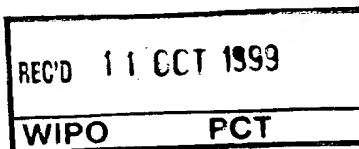
09/763916



INVESTOR IN PEOPLE

GB99/2796

The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ



I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

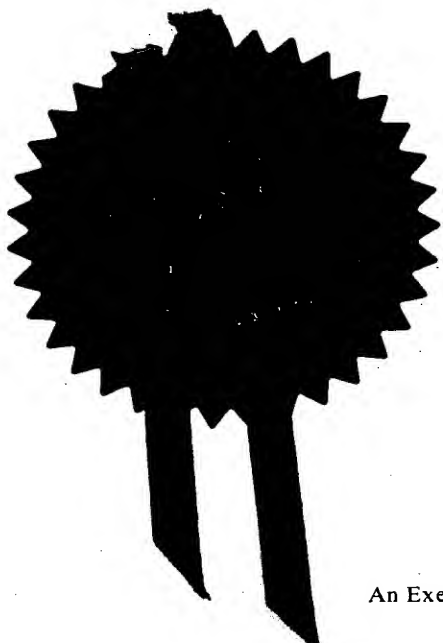
Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules

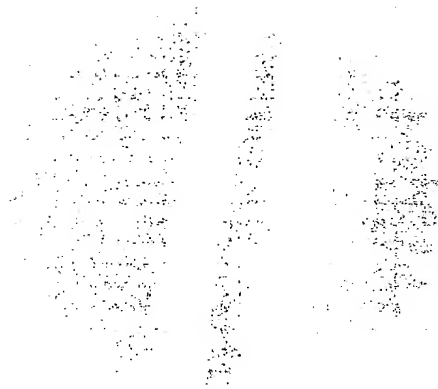
**PRIORITY
DOCUMENT**
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

Signed

Andrew Gorse

Dated 16 September 1999





Request for grant of a patent

See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form.

RECEIVED BY FAX

The Patent Office

Cardiff Road
Newport
Gwent NP9 1RH

Your reference **CRO 50664/GB**

Patent application number **9818778.4** **28 AUG 1998**
(The Patent Office will fill in this part)

Full name, address and postcode of the or of each applicant (underline all surnames)
CROSFIELD LIMITED
4 Liverpool Road
Bank Quay
Warrington
Cheshire
WA5 1AB

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation
7438 275001
UNITED KINGDOM

Title of the invention
Particulate Carrier for Biocide Formulations

Name of your agent (if you have one) **Anthony Robert Collingwood**
"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)
ICI GROUP INTELLECTUAL PROPERTY
INTELLECTUAL PROPERTY DEPARTMENT
PO BOX 11, THE HEATH
RUNCORN, CHESHIRE
WA7 4QE

Patents ADP number (if you know it) **1011485003**

If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number	Country	Priority application number (if you know it)	Date of filing (day / month / year)

If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application	Number of earlier application	Date of filing (day / month / year)

Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

YES

- a) any applicant named in part 3 is not an inventor, or
 - b) there is an inventor who is not named as an applicant, or
 - c) any named applicant is a corporate body.
- See note (d))

Enter the number of sheets for each of the following items you are filing with this form. Do not submit copies of the same document

Continuation sheets of this form

Description

16 / 1

Claim(s)

1 /

Abstract

1 /

Drawing(s)

0. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

1.

I/We request the grant of a patent on the basis of this application.
CROSFIELD LIMITED

Signature *ARC Unghard*
DULY AUTHORISED OFFICER

Date 28/8/98

2. Name and daytime telephone number of person to contact in the United Kingdom

Valerie Ann Moreland
01928 51 1136

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

- 1) If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 300305.
- 2) Write your answers in capital letters using black ink or you may type them.
- 3) If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- 4) If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- 5) Once you have filled in the form you must remember to sign and date it.
- 6) For details of the fee and ways to pay please contact the Patent Office.

Patents Form 1/77

Particulate carrier for biocide formulations

This invention relates to an inorganic particulate carrier particle for use as a vehicle for introducing biocides into liquid-based media such as paints, lacquers, plastisols, oil drilling fluids and surface cleaning compositions. The term "biocide" as used herein is to be understood to refer to agents such as germicides, bactericides, fungicides, algicides and the like, which are used for their ability to inhibit growth of and/or destroy biological and/or microbiological species such as bacteria, fungi, algae and the like.

Biocidal agents (biocides) capable of protecting paint, lacquer, plastisol, oil drilling fluids and surface cleaning compositions are well known in the art. US-A-4129448 and 4166318 are illustrative of prior art disclosing the use of biocides to stabilise mildew growth in acrylic emulsion polymer paints. US-A-3699231 discloses the use of an aldehyde/carbamate mixture to inhibit bacterial growth. Other inhibiting admixtures are known containing isothiazolones and chlorinated derivatives of which US-A-3929561 and US-A-4295932 are examples. All the above disclosures describe a method for protecting the bulk formulation by adding the biocide directly to the composition.

Attempts to control the release of biocide to inhibit bacterial and fungal growth have centred around the use of sol gel chemistry to entrap the biocide but allow release thereof by diffusion from the hydrogel network. This approach is exemplified by EP-A-0602810, EP-A-0736249, GB-A-2235462 and GB-A-1590573 and US-A-5229124. Applications of sol gel entrapment technology for the controlled release of biocide have however been limited owing to the need for the components, that form the encapsulation system "in situ", to be included in a particular formulation and be compatible with the remainder of the ingredients.

Another approach involving the encapsulation of organic liquids such as perfumes, food flavours, pesticides and fungicides is disclosed in US-A-4679779 in which the organic liquid is combined with particles of amorphous silica having a pore size distribution wherein 50% of the integrated micropore volume is constituted by micropores having a radius up to 500 Angstrom Units (AU), the liquid and particles being combined in such a way that droplets of the organic liquid are encompassed within a shell of silica particles. The silicas employed are Tokusil PR and Tokusil NR, made by Tokuyama Soda Co. Ltd. The average particle size and BET surface area for Tokusil PR and Tokusil NR are 100 and 130 microns respectively and 198 and 195 m²/g respectively.

The impregnation of mineral particles with biocides is also known. US-A-4552591 describes a composition intended to protect polymer dispersions used in oil field water treatment. This composition comprises a liquid biocide adsorbed on mineral adsorbents, granular or bead-like in nature, such as diatomaceous earth, silica, metal oxides (alumina bauxite, magnesia iron oxide), clays, zeolites, resins and waxes. Apart from a general reference to "well known adsorbents having a high degree of surface area", no mention is made of key properties such as surface area, pore volume, pore size, pore size distribution. The preferred adsorbent is diatomaceous earth and whilst this material has a high propensity

for liquids, there is no evidence that the carrier particle will retain biocide within its pore system and provide controlled release to an aqueous based composition.

The present invention seeks to provide an improved biocide-carrying carrier particle.

According to one aspect of the present invention there is provided a particulate composition of matter comprising porous inorganic carrier particles having biocide adsorbed within the pore system thereof and having a retention factor (as defined herein) of at least 0.6, preferably at least 0.8.

The retention factor, R, referred to above is determined from the equation $R = A/P$, where A represents the percentage active ingredient by weight remaining in the pore system after contacting with water according to the conditions defined herein and P represents the potency (Minimum Inhibition Concentration in mg of active ingredient per litre) of the biocide determined with respect to the reference microorganism *Aureobasidium pullulans* using the procedure defined herein.

The usefulness of the inorganic carrier particle will depend on the particular biocide being used, its effectiveness at various activity levels and the quantity of biocide (active ingredient) adsorbed and retained in the pore system. The amount of biocide deemed to be effective in the pore system will depend on the potency of the biocide, that is, the minimum concentration of active ingredient to prevent microbial or fungal growth. For the purposes of the present invention, the reference microorganism is *Aureobasidium pullulans*. Commonly used biocides are 2-Octyl-4-Isothiazolin-3-one (OIT) and a blend of 2-Methyl-4-Isothiazolin-3-one (MIT) and 5-Chloro-2-Methyl-4-Isothiazolin-3-one (CIT), known as (CIT/MIT). For these biocides, the Minimum Inhibition Concentration (MIC) is 36 and 5 mg of active ingredient per litre for OIT and CIT/MIT respectively.

Prior to contact with liquid media into which the particles are to be introduced, the particles preferably carry at least 30% by weight of biocide in aqueous solution or water/organic solution.

Such particles will usually be chemically inert with respect to the liquid media into which they are introduced.

A feature of the invention is the ability of the particles, when formulated into solvent or aqueous based compositions, to retain the biocide within the pore system thereof to such an extent that release of the biocide into the liquid media is sufficiently retarded in order to provide an extended period of biocidal, e.g. bactericidal and/or fungicidal, activity.

Preferably the inorganic particles have an activated micropore system. Under the IUPAC system, a micropore is one having a diameter of no more than 30 Å, activation usually being achieved by thermal treatment. Whilst not wishing to be bound by theory it is thought that the carriers that contain an activated micropore system are capable of adsorbing the biocide molecules in preference to water and other substrate molecules.

In order to secure appropriate retention of biocide, a preferred inorganic carrier particle has a pore area of at least 25 m²/g, preferably at least 30 m²/g, more preferably at least 40 m²/g, and up to about 300 m²/g, e.g. 50 m²/g to 250 m²/g, in the pore size range of from about 20 to about 60 Ångströms,

and a BET surface area of at least 200 m²/g and more preferably at least 300 m²/g, typically 350 m²/g to 1200 m²/g.

The porous inorganic carrier particles preferably have a biocide adsorption capacity of at least 10%, more preferably at least 15% and most preferably at least 20% by weight of the carrier particle plus biocide. The adsorption capacity in this instance is the amount of biocide which is retained in the pore system of the porous inorganic carrier particle when the particle containing the biocide is contacted with water as defined herein. The desired biocide adsorption capacity of the carrier particle will, in practice, depend on the particular biocide employed and its potency.

The biocide generally comprises a composition to control and prevent the germination and growth of bacteria, fungi and algae and include the following suitable chemical types: aldehydes, formaldehyde condensates, triazines, phenolics, carbonic acid esters, amides, eg, N'-(3,4-dichlorophenyl)-N,N-dimethyl urea, carbamates, eg, methyl-N-benzimidazol-2-methylcarbamate, thiocarbamates, thiocyanates, dibenzamidine, pyridine derivatives, triazoles, thiazoles, isothiazolones, eg, 2-methyl-4-isothiazolin-3-one, N-haloalkylthio compounds, eg, N-dichlorofluoromethylthiophthalimide and the like. The isothiazolin-3-ones are the presently preferred biocides.

Suitable isothiazolin-3-ones include 2-methyl-4-isothiazolin-3-one, 2-ethyl-4-isothiazolin-3-one, 2-propyl-4-isothiazolin-3-one, 2-butyl-4-isothiazolin-3-one, 2-amy-4-isothiazolin-3-one, 5-chloro-2-methyl-4-isothiazolin-3-one, 5-bromo-2-methyl-4-isothiazolin-3-one, 5-iodo-2-methyl-4-isothiazolin-3-one, 5-chloro-2-butyl-4-isothiazolin-3-one, 5-bromo-2-ethyl-4-isothiazolin-3-one, 5-iodo-2-amy-4-isothiazolin-3-one, 1,2-benzisothiazolin-3-one, 2-n-octyl-4-isothiazolin-3-one, 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one and other similar analogues and homologues within the genus.

Advantageously the biocide is selected from a mixture of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one, typically in the weight ratio of between 1.5 and 2.5:1, e.g. in the range 2.7 to 3:1; 2-n-octyl-4-isothiazolin-3-one; or 4,5-dichloro-2-(n-octyl)-4-isothiazolin-3-one.

The carrier particles suitable may be constituted by amorphous silicas, amorphous aluminas, pseudoboehmites (a form of microcrystalline aluminium hydroxide), Y-zeolites or dealuminated Y-zeolites. In the case of the latter, the Si:Al ratio should be in the range from preferably from about 5:1 to about 33:1.

Absorption of the biocide is usually achieved by mixing the carrier particles with the biocide and such mixing may be carried out in a variety of ways known to those skilled in the art, for example spraying the biocide solution onto the porous inorganic particles in a rotary drum, or while conveyed on a conveyor belt. Non limiting examples of powder mixers include, Neuter conical mixers, double cone mixers, trough mixers, fluid bed mixers and various rotating blade vessel mixers. In all these mixers the powder charge is fluidised by a paddle, screw, air agitation or by mechanical rotation. The biocide solution is sprayed onto the particles and mixing continued until the take-up of biocide solution to the desired level is obtained (usually so that the porous inorganic particles maintain a free flowing

consistency). The biocide/inorganic particle composition can then be dropped by gravity into suitable containers.

The amount of biocide added to the porous inorganic carrier particles will depend on the particular biocide being used and its effectiveness at various activity levels. Thus the concentrated biocide is usually diluted to afford an activity level commensurate with microbial inhibition. Further, a solution 10% by weight biocide in an appropriate solvent (10% active) has biocidal properties which will vary depending on the particular biocide and the amount of the solution which is added to a particular microbial culture. Accordingly, a biocide may be added to the porous inorganic particles undiluted (100% active) or it may be diluted with a solvent to a lower activity (as low as 10% active). This is particularly the case for the isothiazolin-3-ones where the pure biocide is usually diluted with water or water alcohol blends to achieve levels of from about 1 to about 60%, preferably from about 2 to about 50%, e.g. about 5 to about 25%, active by weight.

The biocide-impregnated carrier particles are particularly useful in surface coating and sealant compositions, e.g. paints, lacquers, sealants and plastisols.

According to a second aspect of the invention there is provided a surface coating or sealant composition incorporating a biocide-carrying particles in accordance with said first aspect of the invention.

Typically the composition comprises a film forming material, which is usually polymeric in nature, a solvent and various additives, such as pigments, dyes, dispersing agents, surfactants and antifoaming agents. The total non-volatile content of the composition, usually referred to as the solids content, can vary widely. Often it is desirable that the non-volatile content be at least 30% by weight of the formulation in order that a practical amount of film forming material is present in the dried/cured film. The compositions often can be satisfactorily formulated at a non-volatile content as low as 10% by weight or as great as 100% by weight but, in the latter case, thinning may be necessary at this concentration to provide satisfactory application. The preferred non-volatile concentration is from about 30 to about 65% by weight, irrespective of whether the solvent is organic-based or water.

Where the composition is water based, it generally comprises an aqueous dispersion of the polymer in an emulsion form as the major film forming component whereas a solvent borne composition usually employs the polymer per se, e.g. in solution. Examples of such polymers include homopolymers and copolymers of: (1) vinyl esters of an aliphatic acid having 1 to 18 carbon atoms, especially vinyl acetate; (2) acrylic acid esters and methacrylic acid esters of an alcohol having 1 to 18 carbon atoms, especially methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate and butyl methacrylate; and (3) mono and di-ethylenically unsaturated hydrocarbons, such as ethylene, isobutylene, styrene and aliphatic dienes, such as butadiene, isoprene and chloroprene.

Poly(vinyl acetate) and copolymers of vinyl acetate with one or more of the following compositions: vinyl versatate or vinyl esters of fatty acids having 3 to 18 carbon atoms, vinyl chloride, vinylidene chloride, styrene, vinyl toluene, acrylonitrile, methacrylonitrile, mono or di-fumaric or -maleic acid esters, such as of the alkanols having 1 to 4 carbon atoms, including for example, monomethyl

fumerate, diethyl maleate or fumarate, dibutyl maleate or monobutyl maleate, or one or two of the acrylic and methacrylic esters mentioned above may be used as the film forming components where the paint is aqueous based. Similarly, copolymers of one or more of the acrylic or methacrylic acid esters mentioned above with one or more of the following monomers: vinyl acetate, vinyl esters of higher fatty acids, the mono or di-alkyl esters of itaconic acids, the mono or di-alkyl esters of fumaric acid or the mono or di-alkyl esters of maleic acid, such as esters of methanol ethanol, or butanol, vinyl chloride, vinylidene chloride, styrene, vinyltoluene, acrylonitrile and methacrylic nitrile may be used in the composition according to said second aspect of the invention.

The surface coating or sealant composition can contain additional materials to vary the properties and to adapt the composition for different uses. For example plasticisers can be added together with a range of pigments and dyes. The relative proportions of vehicle to pigment may fall in a wide range, such as from a ratio of 1:20 to 20:1 but for most formulations the range is 1:5 to 5:1. Cellulose derivatives such as methyl cellulose, carboxymethyl cellulose or hydroxyethyl cellulose can be used as bodying agents. Antifoam agents can be included to control foam generation caused by the presence of surfactants to assist the dispersion of pigments and dyes. Other auxiliary materials that may be used include dispersing agents, such as aromatic sulphonates condensed with formaldehyde, humectants such as water soluble gums, glycol laurate, propylene glycol, diethylene glycol and the like, thickeners/body agents, perfume and like materials including neutralising and masking agents which are used to overcome odours or impart pleasant odours; other resinous materials such as drying oils or latices of styrene or of styrene and butadiene.

The amount of porous inorganic carrier containing the biocide incorporated in a surface coating or sealant composition will vary according to factors such as the composition itself, particular inhibitor composition, the conditions of use of solvent, water or polymer dispersion and the extent of prior contamination with micro-organisms, the time period of growth inhibition desired, the requirements of the Health and Safety exposure limits. Usually, to afford adequate protection for many applications, the amount of biocide-containing carrier particle added to the surface coating or sealant composition will be such that the active biocide constitutes from about 0.01% to about 3%, e.g. 0.01% to 2%, by weight of the composition.

The porous inorganic carrier containing the biocide may be incorporated into the surface coating or sealant composition by adding the particulate carrier (i) to water used in the formulation, (ii) to the polymer dispersion or (iii) to the total formulation. This is optimally carried out in a containing vessel which can be readily agitated with a high speed disperser such as a Silverson mixer.

The biocide-containing particles of the invention also have application in surface cleaning compositions in order to enhance the performance of such compositions. Accordingly, in a third aspect of the present invention there is provided a surface cleaning composition incorporating biocide-carrying particles according to said one aspect of the invention.

The surface cleaning composition preferably comprises an aqueous dispersion of a surfactant and an inorganic builder such as an aluminium silicate or zeolite and, optionally, other components such as one or more of the following: water soluble complex formers or precipitating agents for calcium ions; abrasives; water soluble or water dispersible organic solvents; hydrotropes; and soil suspending agents.

Suitable surfactants of the sulphonate type are alkyl benzene sulphonates in which the alkyl group has from 9 to 15 carbon atoms, alkane sulphonates, esters of alpha-sulpho fatty acids, sulphuric acid mono esters of primary aliphatic C_{10} to C_{12} alcohols, sulphated fatty acid alkanol amides, fatty acid mono glycerides with C_{10} to C_{20} fatty acids and sulphates of primary or secondary aliphatic C_{10} to C_{20} alcohols reacted with 1 to 6 moles of ethylene oxide. Surfactants having anionic groups may be present in the form of their sodium, potassium, and ammonium salts or in the form of water soluble salts of organic bases, such as mono-, di or tri ethanol-amine.

Suitable non-ionic surfactants are addition products of ethylene oxide and an aliphatic C_{10} to C_{20} alcohol or an alkyl phenol, fatty amine or fatty acid, ethoxylated products of aliphatic alcohols, C_{10} to C_{20} oxoalcohols and secondary aliphatic alcohols having 12 to 18 carbon atoms. Suitable non-ionic surfactants also include surface active amine oxides such as N-dodecyl-N, N-dimethyl amine oxide, N-tetradecyl-N, N-dihydroxy ethyl amine oxide, N-hexadecyl-N, N-bis (2,3 - dihydroxy-propyl) amine oxide.

In addition to a hydrophobic, generally aliphatic group, suitable zwitterionic surfactants that not only contain hydrophilic acidic groups, but also basic groups are useful. Zwitterionic compounds having four-fold substituted ie: quaternary ammonium group belonging to betaine group can also be formulated into the composition. Particularly useful are the carboxy, sulphonate and sulphate betaines of nitrogen. Typically representative examples of zwitterionic surfactants are compounds of 3-(N-hexadecyl-N, N-dimethylammonio)-propane sulphonate, 3-(N-coconut-alkyl-N, N-bis-(2,3-dihydroxy propyl)-ammonio)-propene sulphonate.

Suitable complex formers or precipitating agents for calcium ions or heavy metal ions include inorganic agents, such as pyrophosphate, tripolyphosphate, higher polyphosphates and metaphosphates, and the organic agents, such as salts of aminopoly-carboxylic acids, for example, nitrile tri acetic acid, ethylene-diamine-tetra-acetic acid, of citric acid, gluconic acid; of carboxy-methyl-ether-carboxylic acids having molecular weights in excess of 350, for example, poly acrylic acid, poly-alpha-hydroxyacrylic acid. Also useful are the water soluble salts of the phosphono-alkane-polycarboxylic acids and the amino-and hydroxy-substituted alkane polyphosphonic acids.

Soil suspending agents that may be employed are generally water soluble colloids, such as water soluble salts of polymeric carboxylic acids, glue, gelatine, salts of ether-carboxylic acids or ether sulphonic acids of starch and cellulose, or salts of acidic sulphuric acid esters of cellulose or starch. Polyamides containing water soluble acidic groups are also suitable for this purpose. In addition, soluble starch preparations and starch products, such as decomposed starches aldehyde starches and polyvinyl pyrrolidone may also be used.

The most suitable organic solvents that may be employed are alcohols and ether alcohols which are water-soluble or can be emulsified with water, for example ethanol, isopropyl alcohol, butanol, amyl alcohol, ethylene glycol, diethylene glycol.

The amount of porous inorganic carrier containing the biocide incorporated in the surface cleaning composition will vary according to factors such as those mentioned previously in connection with surface coating compositions. Typically, a surface cleaning composition according to said third aspect of the invention will incorporate an amount of biocide-carrying particles such that the biocide constitutes about 0.1 to about 3% by weight of the cleaning composition.

The biocide-containing particles may be incorporated into the surface cleaning composition by adding the particulate carrier (I) to the water used in the formulation, (II) to the additive dispersion, or (III) to the total formulation. The addition of the inorganic carrier particulate containing the biocide is optimally carried out in a containing vessel which can be readily agitated with a rotating blade, propellor or turbine.

Definitions and Procedures

The porous inorganic particulate carrier biocide compositions of the invention are defined in terms of the properties and texture of the porous inorganic particulate together with their capability to adsorb biocide and retain it within the specifically selected pore size range.

I) Weight Mean Particle Size

The weight mean particle size of the porous inorganic carrier particulate is determined using a Malvern Mastersizer model X, with a 45mm lens and MS15 sample presentation unit. This instrument, made by Malvern Instruments, Malvern, Worcestershire, United Kingdom uses the principle of Mie scattering, utilising a low power He/Ne laser. Before measurement the sample is dispersed ultrasonically in water for 5 minutes to form an aqueous suspension. This suspension is stirred before it is subjected to the measurement procedure outlined in the instruction manual for the instrument, utilising a 45 mm lens in the detector system.

The Malvern Mastersizer measures the weight particle size distribution of the silica or reference material. The weight mean particle size (d_{50}) or 50 percentile, the 10 percentile (d_{10}) and the 90 percentile (d_{90}) are readily obtained from the data generated by the instrument.

II) BET surface area

Surface area is determined using standard nitrogen adsorption methods of Brunauer, Emmett and Teller (BET), using a single point method with a Sorptly 1750 apparatus supplied by Carlo Erba company of Italy. The sample was outgassed under vacuum at 270°C for 1 hour before measurement.

III) High Performance Liquid Chromatography (HPLC)

High Performance Liquid Chromatography (HPLC) was used to evaluate the concentration of biocide in a solvent system. Typically the sample of biocide in a liquid sample is loaded onto a Nucleosil 10C₁₈ column and eluted along the column at a fixed flow rate by the use of eluting solvents and a pump. As with other chromatographic methods the materials loaded onto the column will pass

through the column packing at different rates. The time at which a material exits the column is known as the retention time and is characteristic of the compound being analysed and the method being used. As the components of the mixture exit the column they are analysed by an accurate internal or external UV/Visible spectrophotometer.

The use of HPLC involves three separate steps. Firstly the mobile phase/diluent has to be selected and then prepared. Choosing the most appropriate solvents is often a matter of trial and error. For OIT, methanol, water and acetic acid in a 65:35:0.2 ratio has been found to be the most suitable, whilst for CIT/MIT, methanol, water and acetic acid in a 65:35:0.4 ratio gives the best result. Preparation of the mobile phase involves adding the relevant quantities of solvent, ensuring complete mixing and then degassing using an ultrasonically agitated bath. The second step is calibration of the HPLC equipment which is achieved by analysing a sample of known composition and concentration. The analytical standard should be prepared using the same mobile phase/diluent as that to be used in the determination. The final step is to produce calibration graphs for the biocides used in the study. This is achieved by preparing samples of known quantities of biocide and obtaining concentration values from the generated chromatograms. These concentration values are then used to plot a calibration graph for each biocide used in the study. Test samples can then be run on the HPLC and the quantity of biocide present in the test solutions derived. This method was used to validate the UV/VIS spectroscopic method referred to below.

iv) UV/VIS Spectroscopy

Second derivative UV-Visible spectroscopy has been employed as an alternative to HPLC for determining the biocide concentration in either water or propylene glycol/water. The advantages of this technique being its simplicity of use and high degree of accuracy. Also single- and multi-component systems can be analysed. The deflections in second derivative spectrum are not proportional to the absorption values in the original spectrum. Rather they are proportional to the slope of the latter providing it was scanned in absorption mode. Positive and negative slopes are shown as positive and negative deflections in the derivatised spectrum. It is the position of the absorption and the relation of the extremes which are of interest in this method. Its application here was as a means of monitoring the amount of biocide leached into a solvent and as such the procedure used to evaluate the results was to measure the amplitude of deflection (ΔA) on a peak to peak basis. In this method, the absolute distance between a maximum and an adjoining minimum is determined as a characteristic of the species under investigation. This distance is then compared with a standard calibration to attain the concentration of the sample. A Perkin-Elmer Lambda 7 spectrophotometer was used in conjunction with the Lambda 16 WINDOWS software package to determine accurate values of (ΔA) from the derivative spectra obtained. The software package can be obtained from Perkin Elmer of Post Office Lane, Beaconsfield, Bucks HP9 1QA, United Kingdom.

v) Pore area in a pore size range

Nitrogen adsorption Isotherm is determined using a multi-point method with ASAP 2400

apparatus supplied by Micrometrics of the USA. The samples are outgassed under vacuum at 270 °C for at least one hour before measurement. This apparatus also enables the pore size distribution from the adsorption branch of the isotherm to be calculated. This can be expressed in terms of the cumulative pore area contained in a given range of pore size. The pore area within the pore size range 20 to 50 Angstroms can be readily derived.

vi) Leaching

In this work the biocide carrier particles were added to water in the ratio of 0.3:1 biocide carrier to water. An amount of this blend was chosen to ensure that when it was added to 1000 ml of water the solubility maximum for OIT of 400 ppm would not be exceeded. CIT and MIT are both more water soluble than OIT.

The method employed was as follows: 0.75 g of biocide was added to 2.5 g of carrier material. This was then transferred to a vessel and homogenised by rotating the vessel on rollers for 8 hours. The homogenised blend was then charged into 1000 ml of distilled water, stirring continuously. Aliquots of the slurry were taken at intervals of 0.5, 1, 2, 4, 6, 12, 30, 60 and 90 minutes and it was established that after 60 minutes the elution curve plateaued and to ensure that equilibrium had been secured, the experimental work was conducted using a 90 minute equilibrium time. These were filtered and diluted to a concentration within the range of the calibration curve for the respective biocide under investigation. The samples were then analysed by 2nd derivative UV/VIS spectroscopy as described above.

vii) Fungicidal Assessment Of Coatings

This method was developed so that fungicidal activity of a biocide within a coating could be evaluated. It can be used to investigate the effects of, for example, water leaching, film weight and concentration on the diffusivity of the biocide.

Coatings with and without the biocide were brush applied in two separate coatings (24 hours between each coating) to one side of rubber discs (3.7 cm in diameter). Once dry, the discs were immersed in 30ml of sterile distilled water for 1 hour and then dried in a laminar flow cabinet overnight. Potato dextrose agar plates in Petri dishes were prepared, dried and separately inoculated with 1ml of spore suspensions containing ca 10⁶ cfu/ml of each test fungus. Four fungal species were included in the study: *Aureobasidium pullulans* (FS103), *Rhodotorula rubra* (FS83), *Cladosporium cladosporioides* (IMI71749R) and *Alternaria alternata* (IMI78517). The suspensions were allowed to adsorb into the agar to remove surface wetness. The coated discs were then placed, with coated face down, at the centre of the agar carrying Petri dish. The assembly of plate/disc was then stored in refrigerator for 24 hours to allow diffusion of the biocide to occur. The plates were subsequently placed in an incubator at 25 °C for 5 days. Zones of inhibition were calculated by summing the radial distances as measured from the edge of the filter paper to the fungal growth front at diametrically opposite locations of the disc.

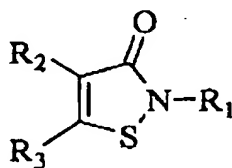
viii) Minimum Inhibition Concentration

The minimum inhibition concentration (MIC) is a measure of the potency of a biocide and comprises the minimum concentration (ppm) of a biocide active or formulation (normally quoted in terms of the active ingredient) determined experimentally *in vitro* to prevent the growth of a pure culture of a reference microorganism. Although the experimental design may differ, as there are no standard methods, the general principles of the necessary procedures remain the same.

A standardised culture of the microbe under test is prepared. Aliquots are added to a suitable liquid nutrient medium in stoppered glass tubes containing a range of concentrations of the biocide active. The mixtures are incubated at a standard controlled temperature to encourage growth of the microbes for a standard time, usually between 24 to 48 hours. The tubes are removed and assessed for growth/no growth by measuring the increase in the optical density of the medium caused by an increase in the number of microorganisms present. Other detection methods such as total viable counts or visual examination may be used. The concentration at which no growth is detected is the minimum inhibition concentration (MIC) for that particular biocide and reference organism. The measurements can be refined by repeating the test using intermediate concentrations of the biocide, between those already chosen as being representative of the killing range, in order to more accurately define the MIC.

Specific Description Of The Invention

The following examples serve to illustrate but not limit the present invention. In all the examples, unless otherwise stated the following biocides have been used. The definition of isothiazolone biocide as used here corresponds to the general structural formula shown below.



4-R₂-5-R₃-2-R₁-4-Isothiazolin-3-one

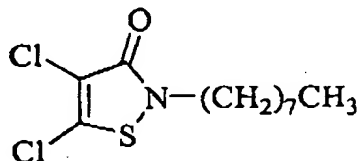
R₁ is an alkyl group with the formula $-(CH_2)_nCH_3$ where $n = 1$ to 8

R₂ can be either H or Halogen, and

R₃ can be either H or Halogen

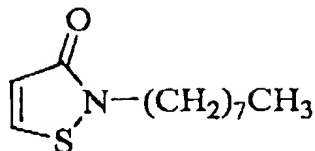
Some examples of this class of compounds are included below

DCOIT



4,5-Dichloro-2-Octyl-4-Isouthiazolin-3-one (DCOIT)

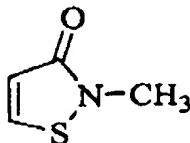
ACTICIDE® 45 - OIT



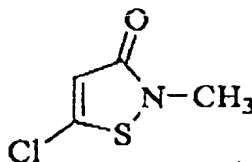
2-Octyl-4-Isothiazolin-3-one (OIT)

46.9 % OIT In Propylene Glycol

ACTICIDE® 14L - CIT/MIT



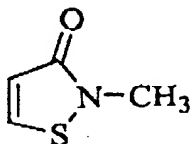
2-Methyl-4-Isothiazolin-3-one (MIT)



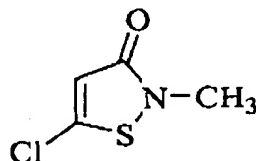
5-Chloro-2-Methyl-4-Isothiazolin-3-one (CIT)

10.3 % CIT / 3.8% MIT (14.1 % Active), in Water

ACTICIDE® TL666 - CIT/MIT



2-Methyl-4-Isothiazolin-3-one (MIT)



5-Chloro-2-Methyl-4-Isothiazolin-3-one (CIT)

2.5 % or less Active in glycol as a ratio of 3:1 CIT/MIT

Example 1

To allow screening tests to be conducted on a small laboratory scale the blocide impregnated inorganic particulate carriers hereinafter described were made by adding the appropriate amount of blocide dropwise, 0.7g of blocide to 2.5g of carrier material, and then homogenised by rotating the vessel containing the blend on rollers for 8 hours. The impregnated inorganic particulate carrier particles were then charged into 1000ml of distilled water and allowed to equilibrate for 90 minutes

under stirring. The suspension was filtered and the level of biocide analysed in the filtrate using 2nd derivative UV/VIS spectroscopy as previously described. By simple difference the % retained by the carrier could be calculated. The results obtained for the carrier materials impregnated with OIT are given in Table I.

Table I

Sample No.	Material	Si:Al Ratio	B.E.T. Surface Area m ² /g	Average Particle Size microns	OIT Retention % By Weight
SD1866	Amorphous Silica		728	4.6	14
SD1866(c)	Amorphous Silica		562	4.3	74
SD1913	Amorphous Silica		395	6.2	5
SD1913(c)	Amorphous Silica		368	6.5	42
SD1868	H-Y Zeolite	5.3:1	581	4.4	27
SD2209	Y-Zeolite dealumntd.	33:1	733	5.6	99
SD1867	4A-Zeolite	2.0:1	20	1.5	0
SD2006	H-Y Zeolite	5.2:1	600	3.5	33
SD2210	Hydrotalcite		178	9.3	10
Cellite 545	Diatomaceous Earth		<10	57	0

The materials labelled SD are inorganic materials available from Crosfield Ltd., Warrington, England. The suffix (c) denotes the material has been heat treated for 2 hours at 700°C. Cellite 545, which is referred to in US-A-4552591, is a commercially available product available from World Minerals, Cellite UK Limited of Livingstone Road, Hessle, Hull, North Humberside, HU13 OEG. It can be seen that Cellite 545 has no affinity for the biocide and is equally as ineffective at retaining the biocide as 4A zeolite and hydrotalcite and many others which are not reported in Table 1. In contrast, the H-Y zeolite, the dealuminated form of Y-zeolite and the heat treated amorphous silicas SD1866(c), SD1913(c) all have a significant propensity to adsorb and retain OIT.

Example 2

Those carrier particles which, from Example 1, were found to exhibit the highest retention of OIT were also investigated for their capability to adsorb CIT/MIT, a higher potency biocide than OIT, and were compared with Cellite 545 and 4A-zeolite. To obtain information on the micropore system present in the materials investigated, nitrogen adsorption isotherms were determined to allow calculation of the pore area within the micropore size range of 20 to 50 angstroms. In Table II, the micropore area is listed together with the retention values for OIT and CIT/MIT. In addition, to distinguish between the retention values of the biocides and their potencies, a Retention Factor R has been calculated for the materials investigated. The Retention Factor R is the quotient A/P of the % of active ingredient A by weight remaining in the pore system after contacting with water under the conditions prescribed and the potency P of the biocide as measured on the basis of the reference microorganism, *Aureobasidium pullulens*, in terms of the Minimum Inhibition Concentration (MIC), which for OIT and CIT/MIT is 36 and 5 mg/l respectively.

Table II

Sample No.	Pore Area m ² /g 20 to 50 Angstroms	OIT Retention % by weight	CIT/MIT Retention % by weight	Retention Factor R OIT	Retention Factor R CIT/MIT
SD1868(c)	211	74	15	2.05	3
SD1913(c)	48	42	15	1.2	3
SD1868	38	27	0	0.75	0
SD 1867 (4A-zeolite)	0	0	0	0	0
SD2209	64	99	15	2.75	3
SD2208	48	33	0	0.92	0
Cellite 545	0	0	0	0	0

It can be seen from Table II that those materials identified for their good retention of biocide in Example 1 have a Retention Factor R in excess of 0.6 for the two biocides, compared with the prior art materials Cellite 545 and 4A-zeolite for which the value is zero. The retentive materials were found to have pore areas in the pore size range 20 to 50 Angstrom of greater than 35 m²/g indicating their potential for controlled release of biocide into a substrate, such as a paint or lacquer system.

Example 3

To produce larger samples of the biocide impregnated inorganic carriers for testing in paint formulations the following method was utilised. The appropriate amount of biocide was added dropwise to the inorganic particulate carrier (500g) whilst it was being stirred in a Sirman SV8 Food Processor (available from Metcalf catering Equipment, Bleanau Ffestinlog, Gwynedd, Wales) so that

the finished product contained 27% by weight of the biocide. The biocide impregnated particulate carrier composition was then sealed in a tin to prevent the loss of volatile components and to allow the blend to equilibrate before mixing into a paint system. The following method was used to disperse the biocide carrier composition in the paint formulation.

The appropriate amount of the biocide carrier composition needed to yield a dry film concentration of 100ppm for CIT/MIT and 600ppm for OIT, was added to 1kg of the paint formulation retained in a suitably sized vessel to allow the dispersion to be agitated with a Cowles high speed disperser. This premix was then transferred to a Silverson type mixer, fitted with a medium mixing head, and mixed until a finer dispersion was obtained. Control formulations containing only (i) the free biocide and (ii) free biocide plus unloaded inorganic carrier particles were prepared in exactly the same way so as to eliminate the method of dispersion as a variable. For each preparation, during dispersion on the Silverson Mixer, the temperature of the vessel was controlled between 40 to 50°C. The two model paint formulations, one a water-borne acrylic and the other a solvent-based alkyd used in this Example had the following compositions:

Solvent-based alkyd

	% By Weight
White Spirit	19.5
Urethane Alkyd (55% in white spirit)	78.2
Cobalt Drier	0.4
Zirconium Drier	0.4
Calcium Drier	0.8
Methyl Ethyl Ketoxime	0.1
Defoamer	0.6

(Urethane Alkyd as supplied under the trade name Unithane 655W by Cray Valley of Waterloo, Machen, Newport, Gwent NP1 8YN, UK)

Water-borne acrylic

Acrylic emulsion

Dispelair CF269 added as required to counteract foaming

(Acrylic emulsion as supplied, devoid of protective biocidal additive, under the trade name Revacryl 1A by Harlow Chemical Co. and Dispelair CF269 defoamer supplied by Blackburn Chemicals)

The biocidal efficacy in the above paint formulations of the range of carriers loaded with OIT or CIT/MIT were compared with the biocides in non-loaded systems. A rapid screening test using *Cladosporium cladosporioides* was used to determine the zones of inhibition around cured, painted rubber discs placed, coated face down, on a solid agar surface seeded with the fungus as described hereinbefore. Tables III and IV summarise the data obtained on the water-borne acrylic and the alkyd paint systems containing free OIT, added only as the biocide to the paint formulation (Free), OIT

loaded onto the carrier (SDno.(L)) and free OIT together with the unloaded inorganic carrier (Free+SDno.). SDno denotes the SD number of the inorganic carrier as listed in Tables III and IV. To highlight distinguishing features in performance, the concentration of OIT in the paint film ranged from 600 to 12000ppm for both the acrylic and the alkyd paint system, irrespective of the method of addition of the biocide to the formulation.

Table III-Acrylic Paint Formulation

Paint Formuln.	OIT Concn. ppm	Addition Method	Zone Present	Zone Size mm
P1	600	Free	+	< 1
P2	1000	Free	+	< 1
P3	2000	Free	+	7
P4	4000	Free	+	10
P5	8000	Free	+	18
P6	12000	Free	+	20
P7	600	SD2209(L)	+	< 1
P8	1000	SD2209(L)	+	< 1
P9	2000	SD2209(L)	+	3
P10	4000	SD2209(L)	+	9
P11	8000	SD2209(L)	+	13
P12	12000	SD2209(L)	+	18
P13	600	Free + SD2209	+	< 1
P14	1200	Free + SD2209	+	< 1

Table IV-Alkyd Paint Formulation

Paint Formulation	OIT Concn. ppm	Addition Method	Zone Present	Zone Size mm
P15	1200	Free	+	< 1
P16	2000	Free	+	2
P17	4000	Free	+	3
P18	8000	Free	+	5
P19	12000	Free	+	10
P20	1200	SD2209(L)	+	< 1
P21	2000	SD2209(L)	+	1
P22	4000	SD2209(L)	+	3
P23	8000	SD2209(L)	+	4
P24	12000	SD2209(L)	+	5

The "zone sizes" referred to above are the summed radial distances, as previously mentioned.

In Tables III and IV, "+" indicates that there was an observable zone of fungal inactivity around the periphery of the painted disc. It can be seen that under the test conditions the response for OIT is not significant in the concentration range 600 to 1,000ppm in either paint formulation. To measure the levels of inhibition imparted by the biocide, concentrations in the paint film needed to be increased to values in excess of 1,200ppm and, in the range 1,200 to 12,000 ppm, it is possible to see differences produced by the different modes of introducing the biocide into the paint formulation. In both formulations there is clear evidence that incorporation of biocide to the paint system adsorbed in the pore system of the inorganic particulate carrier is slowing down the response for OIT, as can be seen by comparing the size of the zones of inhibition for the paint formulations containing high concentrations of biocide. For the alkyd system at a loading of 12000ppm of OIT there is marked reduction in the zone width, from 10 to 5mm, between the paint formulation containing free biocide and the one where the biocide has been added adsorbed in the pore system of the inorganic particulate carrier. For the water borne acrylic the difference in zone widths is not as marked (20 mm compared with 16mm for paint formulations containing 12000ppm of OIT) but in general on comparing the inhibition zones obtained for the range for the formulations containing 2000 to 8000ppm there is sufficient evidence to support the observation that, in this paint system, the response is being slowed by incorporating the biocide on the inorganic particulate carrier.

CLAIMS

1. A particulate composition of matter comprising porous inorganic carrier particles having biocide adsorbed within the pore system thereof and having a retention factor (as defined herein) of at least 0.6.
2. A composition as claimed in Claim 1 in which the retention factor is at least 0.8.
3. A composition as claimed in Claim 1 or 2 in which the particles carry at least 30% of biocide solution.
4. A composition as claimed in any one of Claims 1 to 3 in which the particles have an activated micropore system.
5. A composition as claimed in any one of Claims 1 to 4 in which the particles have a pore area of at least 25 m²/g in the pore size range of from about 20 to about 50 Angstroms.
6. A composition as claimed in any one of Claims 1 to 5 in which the particles have a BET surface area of at least 200 m²/g.
7. A composition as claimed in any one of Claims 1 to 5 in which the particles have a BET surface area of at least 300 m²/g.
8. A composition as claimed in any one of Claims 1 to 7 in which the particles have a biocide adsorption capacity of at least 10% by weight.
9. A composition as claimed in any one of Claims 1 to 8 in which the particles are constituted by amorphous silicas, Y-zeolites or dealuminated Y-zeolites, or a mixture of two or more of these materials.
10. A surface coating formulation incorporating the particulate composition as claimed in any one of Claims 1 to 9.
11. A formulation as claimed in Claim 10 in the form of a paint or lacquer.
12. A formulation as claimed in Claim 10 in the form of a water-based or organic solvent-based paint.
13. A sealant formulation incorporating the particulate composition as claimed in any one of Claims 1 to 9.
14. A surface cleaning composition incorporating the particulate composition as claimed in any one of Claims 1 to 9.

END

ABSTRACT OF THE DISCLOSURE

Particulate carrier for biocide formulations

A particulate carrier material is impregnated with a biocidal formulation and serves as a vehicle for introduction of the biocide into a liquid-based media, such as a surface coating or surface cleaning compositions, in order to allow controlled release of the biocide to combat bacterial, fungal, algal or like growth for an extended period of time.